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Hydraulic Characteristic of Collagen

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Abstract

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The hysteresis of a hydraulic characteristic while pumping an aqueous solution of collagen through a pipe at gradually increasing and decreasing flow rates (hysteresis means that the pressure drop curve during increased flow rate is above the pressure drop during decreasing flow rate) was observed. The problem was initiated by industry and by demand for an on-line recording of rheological properties of collagenous material used for extrusion of collagen casings. The Herschel-Bulkley rheological model was capable to describe rheograms in a wide range of deformation rates; however it was not able to describe and explain the hysteresis. As a possible reason thixotropic properties were identified and the hydraulic characteristic was calculated using a thixotropic generalisation of the Herschel-Bulkley model. The developed 1D numerical model can be applied for on-line modelling of transient flows of incompressible thixotropic food materials (startup flow) and at a limited range of flow rates it is also capable to describe the hysteresis of hydraulic characteristics.

Keywords: thixotropy; collagen; unsteady flow in pipe; hydraulic characteristics

Nomenclature: a – coefficient of structure regeneration (s^{-1}); b – coefficient of structure breakdown (s^{m-1}); K – consistency coefficient ($Pa{\cdot}s^n$); ΔK – increment of consistency coefficient ($Pa{\cdot}s^n$); L – length of pipe (m); m – breakdown index (–); n – flow behaviour index (–); p – pressure (Pa); r – radial coordinate (m); R – radius of pipe (m); t – time (s); u – axial velocity (m/s); $\dot{V}$– volumetric flow rate (m^3/s); x – axial coordinate (m); $\dot{\gamma}$ – shear rate (s^{-1}); λ – structural parameter (–); ρ – density (kg/m^3); τ_w – wall shear stress (Pa); τ_y – yield stress (Pa); $\Delta\tau_y$ – increment of yield stress (Pa)
subscripts: i – index of cross-section (axial coordinate); w – wall

Non-Newtonian fluid flow behaviour (typical for long chain viscoelastic polymers) was deeply described by Bird *et al.* (2002). One of the extreme differences in rheological behaviour is the fluid thixotropy defined initially as a reversible sol-gel transformation (thixotropic substance is an elastic solid, gel, bellow a threshold yield stress, and viscous solution above the threshold). Thixotropy is now viewed as a more general property of non-Newtonian fluids having viscous characteristics that depend on deformation history (apparent viscosity depending upon the time course of previous deformation rate), see review articles by Mewis (1979) and Barnes (1997). Analytical approximations of steady-state hydraulic characteristics (relationships between pressure drop and flow rate) of thixotropic liquids flowing in a straight pipe were presented by Šesták and Žitný (1976), Kemblowski and Petera

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(1981), and Schmitt *et al.* (1998). All these solutions assumed a power-law radial velocity profile independent of the axial position in the pipe. The Finite Element Method (FEM) used by Šesták *et al.* (1990) was a step forward in describing varying radial velocities and structural parameter profiles based on the Houska constitutive model (see Šesták *et al.* 1983); however, the FEM solution was again restricted to stationary cases only. Probably the most complex computational fluid dynamic (CFD) solution using the Houska model, generalised for compressibility and temperature dependence, has been under intensive development in recent years by Wachs *et al.* (2009) and Negrão *et al.* (2011). The CFD techniques used by Wachs and Negrao were based on the method used for a compressible non-Newtonian fluid (Bingham compressible fluids), Vinay *et al.* (2006, 2007), and can be characterised as follows: control volume method (2D orthogonal staggered grid with shifted control volumes for axial and radial velocities), pressure calculated using the augmented Lagrangian multiplier method, and the solution of the resulting saddle point problem using the Uzawa algorithm.

The approximate 1D method suggested in this article is restricted to incompressible liquids but it is much simpler and easier to use. This method is suitable for modelling not only a steady but also start-up and displacement flows in food industry production lines [for example yoghurt – Schmitt *et al.* (1998), and collagen]. Collagenous materials exist in many forms and composition with cross-linking agents, for example glutaraldehyde or polyvinyl alcohol. These materials are used for extrusion of vascular grafts in biomedicine (Kumar *et al.* 2013) or as sausage casings in the food industry (Deiber *et al.* 2011). Nevertheless, information on rheological properties is restricted due to problems with the application of rotational rheometers (wall slip effects and a discharge of tested samples from the gap between cone and plate or plate and plate geometries). Usually only the hydraulic characteristics measured by extruders or capillary rheometers are available giving information on steady shear properties but nothing about thixotropy (hydraulic characteristics are represented by a set of datapoints ($\dot{V}$, Δp), where each point is usually evaluated only at a steady state, when memory effects are suppressed and phenomena like hysteresis cannot be observed). The only exception is a paper by Deiber *et al.* (2011) reporting the thixotropy of collagen suspensions at a low concentration (0.5–3.7%) using a rotational rheometer and a cone and plate configuration.

The problem of transient hydraulic characteristics and hysteresis was initiated by industry and by demand for an on-line recording of rheological properties of collagenous material used for extrusion of collagen casings. Motivation came from the hysteresis of hydraulic characteristic observed while pumping a collagenous polymeric material through a pipe at gradually increasing and decreasing flow rates. This arrangement was designed for quick identification of the Herschel-Bulkley rheological model of processed material. The Herschel-Bulkley model assumes that the shear properties depend only upon the actual flow rate and not upon the entire deformation history of fluid particles, therefore not upon previous flow rates. However, the pressure drop recorded during increasing flow rates of collagen was always greater than that during decreasing flow rates at the same flow rate. Hydraulic characteristics (pressure drop versus flow rate) were no longer unique functions $\Delta p(\dot{V})$ but formed slim hysteresis loops. It should be emphasised that this is quite a different phenomenon from the hysteresis curves recorded when measuring the same thixotropic samples in a rotational rheometer, see for example Deiber *et al.* (2011) (this situation is much simpler because the thixotropic structure in rotational rheometers is homogeneous and depends only upon time and not upon space). The suggested simple thixotropic model that describes the evolution of structural changes over time and space is, in principle, capable of predicting hysteresis features, even in the nonhomogeneous pipe flow.

The aim of this paper is to explain the observed experimental data by application of the simplest rheological model of the thixotropic behaviour.

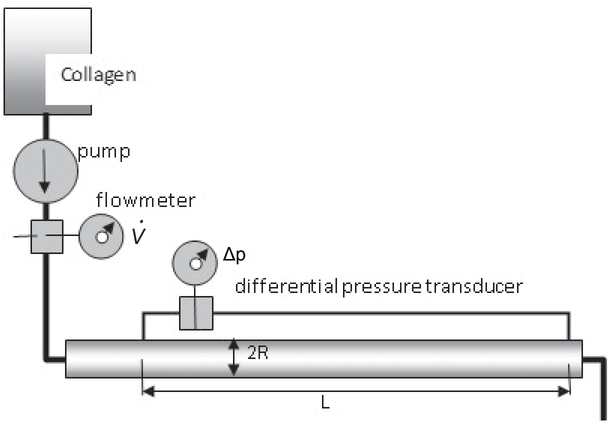

Figure 1. Setup of an experimental pipeline

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MATERIAL AND METHODS

Experimental. The experimental equipment (Figure 1) is a part of the production extrusion line. Processed material (collagenous matter: 7.1% mass fraction of bovine collagen + special additives + water) is delivered from a storage tank by an AQM 57-20/S003 (AQ Pumpy, Hranice, Czech Republic) positive displacement reciprocating pump, through a relatively long straight pipe (L = 4.287 m, R = 0.0106 m) to an extruder. The influence of this pump on the material structure is neglected. Flow rate is controlled by varying the speed of the pump and derived from pump revolutions and represents the exponential function of time. Pressure drops (changes) are recorded by DMP 331P (BD Sensors GmBH, Thierstein, Germany) pressure transducers and temperatures are monitored using RTD thermometers (Hans Turck GmbH&Co. KG, Mülheim an der Ruhr, Germany). All data were collected and processed using a process control computer. Sensors were calibrated: error of the pressure transducer was less than 3%, and error of the flowmeter was less than 2%. Special experiments characterised by a gradual increase and decrease of mass flow rate at constant temperature and constant composition of tested matter were carried out during a break of production in the extrusion processing line with the goal of identifying parameters for the Herschel-Bulkley rheological model.

Processed material, at relatively high concentrations of bovine collagen (7.1%), is a paste that looks like "silly putty". Laboratory tests of several collagen samples carried out by using size exclusion chromatography and UV detection identified distribution of molecular mass and three characteristic fractions (12% of light fraction 3 kDa, 15% of middle fraction 550 kDa, and 19% of the longest fraction 780 kDa). Our preliminary experiments in the laboratory confirmed linear viscoelasticity at small deformations. The cone and plate geometry applied on an oscillating rheometer Haake RheoStress RS-150 (Thermo Fisher Scientific, Karlsruhe, Germany) provided moduli values G' ~ 5 kPa, G" ~ 2 kPa.

We have done extra experiments using parallel plate geometry and constant angular velocity with the aim to identify time constants of thixotropic structure decay and restoration. No matter that a raw emery paper was bonded to both disc plates, the collagen samples were expressed from the gap when the rotation of the top plate started. The momentum decreased very quickly and measurement was impossible to reproduce.

Constitutive equation. The Houska model (Šesták *et al.* 1983) of thixotropic fluids is a straightforward generalisation of the routinely used Herschel-Bulkley constitutive equation (the combination of a power-law liquid with consistency coefficient K and flow behaviour index n and a Bingham liquid with yield stress τ_y), simplified for the special case of unidirectional simple shear flow to a scalar equation for shear stress τ:

$$\tau = \tau_y + \Delta\tau_y\lambda + (K + \Delta K\lambda)\dot{\gamma}^n \qquad \dot{\gamma} = \frac{\partial u}{\partial r} \tag{1}$$

The structural parameter $\lambda = 1$ describes a fully recovered internal structure (and high consistency of the liquid), while $\lambda = 0$ corresponds to a completely destroyed internal structure (with minimum consistency K and yield stress τ_y). Time changes for structural parameter λ are described by the transport equation:

$$\frac{D\lambda}{Dt} = a(1 - \lambda) - b\lambda\dot{\gamma}^m \tag{2}$$

Model parameters a and b characterise time constants of regeneration and structure destruction.

***Solution of unsteady flow of thixotropic liquid in a pipe*.** The following simplified numerical solution neglects inertial effects due to very high viscosity of the collagen material and relatively slow flow rates (range of low Reynolds numbers). More restrictive is the assumption that the structural parameter λ depends only on the axial coordinate and time $\lambda(t, x)$. This case is probably more relevant for long and highly entangled polymeric chains (let us mention the fact that the tested collagen is characterised by extremely long chains with molecular mass of 770 kDa).

If λ is independent of the radial coordinate, then the effective consistency K^* and the yield stress τ_y^* are dependent only upon time and the axial coordinate:

$$K^* = K + \lambda\Delta K \qquad \tau_y^* = \tau_y + \lambda\Delta\tau_y \tag{3}$$

Therefore, it is possible to use the RMW (Rabinowitsch, Mooney, Weissenberg) equation for volumetric flow rate expressed as a function of wall shear stress (or gradient of pressure):

$$\frac{\dot{V}}{\pi R^3} = \left(\frac{\tau_w}{K}\right)^{\frac{1}{n}} \left(\frac{n}{3n+1}\left(1-\frac{\tau_y^*}{\tau_w}\right)^{\frac{3n+1}{n}} + \frac{2n}{2n+1}\frac{\tau_y^*}{\tau_w}\left(1-\frac{\tau_y^*}{\tau_w}\right)^{\frac{2n+1}{n}} + \frac{n}{n+1}\left(\frac{\tau_y^*}{\tau_w}\right)^2\left(1-\frac{\tau_y^*}{\tau_w}\right)^{\frac{n+1}{n}}\right) \tag{4}$$

Because we need to calculate the wall shear stress for a given flow rate, it is necessary to iterate the inverse relationship:

$$\tau_w = \tau_y^* + K^*\left(\frac{\dot{V}}{\kappa(\tau_w)\pi R^3}\right)^n$$

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$$\kappa(\tau_w) = \frac{n}{3n+1}\left[1 - \frac{1}{2n+1}\frac{\tau_y^*}{\tau_w} - \frac{2n}{(2n+1)(n+1)}\left(\left(\frac{\tau_y^*}{\tau_w}\right)^2 + n\left(\frac{\tau_y^*}{\tau_w}\right)^3\right)\right] \quad (5)$$

After just a few iteration steps, the iteration process converges independently of (*i*) yield stress, (*ii*) the flow behaviour index, and (*iii*) consistency.

Evolution of the cross-section averaged structural parameter λ is described by the transport Eq. (2) integrated across the cross-section of the pipe. The last term describing the averaged decomposition of structure can be expressed in an analytical form, because the radial velocity profile is known:

$$\dot{\gamma}^m = \frac{2}{R^2}\int_{r_y}^{R} r\left(\frac{\tau_w \frac{r}{R} - \tau_y^*}{K^*}\right)^{\frac{m}{n}} dr = \frac{2n(\tau_w - \tau_y^*)^{\frac{m}{n}+1}}{\tau_w^2 K^{*\frac{m}{n}}}\frac{(m+n)\tau_w + n\tau_y^*}{(m+2n)(m+n)} \quad (6)$$

The transport equation (2) is a hyperbolic equation that can be integrated analytically along its characteristic $dx = u\,dt$ giving:

$$\lambda(t) = \frac{a - (a - (a + b\dot{\gamma}^m)\lambda_0)e^{-(a+b\dot{\gamma}^m)(t-t_0)}}{a + b\dot{\gamma}^m} \quad (7)$$

where: $\lambda(t)$ – value of the structural parameter of a fluid particle having a value of λ_0 at time t_0, assuming that the particle is under the influence of a constant shear rate (constant flow rate) within the time interval (t_0, t).

In cases with variable flow rates, it is necessary to apply Eq. (7) using shorter time steps during integration.

The 1D numerical solution by the method of characteristics calculates nodal values of structural parameters at a new time $t^{(k+1)}$ from the values of the structural parameter $\lambda_1^{(k)}, \lambda_2^{(k)}, \ldots$ at equidistant nodes ($x_1 = 0$, $x_2 = \Delta x$, $x_3 = 2\Delta x$, ...) and previous time $t^{(k)}$. The time step $\Delta t^{(k)} = t^{(k+1)} - t^{(k)}$ is not a constant and is determined by the volumetric flow rate so that the fluid particle moves a distance Δx:

$$\Delta t^{(k)} = t^{(k+1)} - t^{(k)} = \frac{\Delta x}{\bar{u}^{(k)}} = \frac{\Delta x \pi R^2}{\dot{V}^{(k)}} \quad (8)$$

(Courant-Friedrichs-Lewy criterion CFL = $u(\Delta t/\Delta x) = 1$)

The new value of $\lambda_i^{(k+1)}$ is calculated by integration of a fluid particle along the characteristic from the old value $\lambda_{i-1}^{(k)}$ using Eq. (7). After the new values for structural parameters are updated, wall shear stress can be calculated from Eq. (5) and pressure gradient from Eq. (9) which follows from the balance of forces assuming negligible inertial forces (this equation is independent of rheology and velocity profiles):

$$\frac{\partial p}{\partial x} = \frac{2\tau_w}{R} \quad (9)$$

Overall pressure profile is obtained by integration of pressure gradients at each time step.

Implementation is very simple (e.g. using the Matlab program) and no problems with convergence or stability were encountered. Simplified flowchart, including optimisation of rheological parameter by comparison with experimental data, is presented in Figure 2.

RESULTS AND DISCUSSION

Figure 3 presents data obtained from a production line with the collagen material using the experimental setup described in paragraph *Experimental*. After start up the production line a very small volumetric flow rate a 7×10^{-7} m^3/s was adjusted and maintained constant for a few minutes (unfortunately pressures in this part were not recorded; and only the model prediction, is represented by a short vertical line at the flowrate 7×10^{-7} m^3/s, is shown in Figure 3). Afterwards the volumetric flow rate was gradually increased from 7×10^{-7} m^3/s up to 5.1×10^{-5} m^3/s, and back to 7×10^{-7} m^3/s. The rate of volumetric change was rather slow (20 min up and 20 min down). Such a slow variation of flow rate increases the number of time steps (4100 time steps for 151 grid points in the axial direction) and increases the run-time necessary for preliminary identification of thixotropic model parameters. The parameters (a, b, n, m, K, ΔK, τ_y, $\Delta\tau_y$) were identified (approximately) by linear search in parametric space using the least square criterion (sum of squares of deviations between measured and predicted pressures during up and down phases, see flowchart in Figure 2). The direct search is realised by a time consuming evaluation of all combinations of eight parameters (a, b, m, ...) with specified ranges and increments (the ranges were several times modified manually with the aim to increase resolution and accuracy of optimal parameters).

It is obvious that the model of thixotropy is not able to describe the hysteresis at high flow rates, a trend that was also observed in other simulations. The fact that the hydraulic hysteresis of thixotropic liquid is significant only at low flow rates is closely related to the residence time of fluid particles and can be explained in the following way: the fluid particle leaving the pipe has a structure corresponding to the

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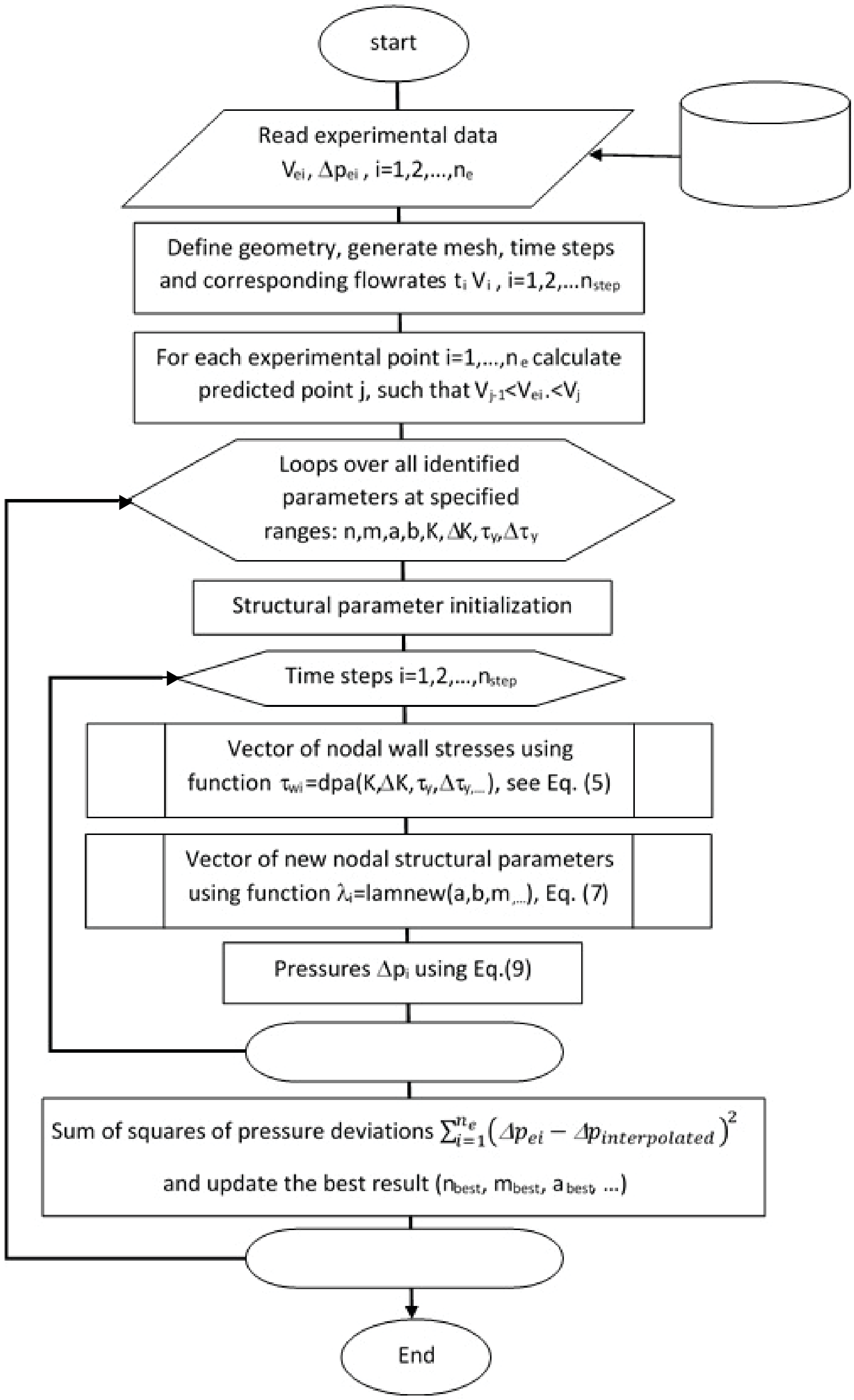

Figure 2. Flowchart of 1D simulation with optimisation of rheological parameters

mean intensity of destruction during the trajectory from inlet to outlet. In the up-phase (increasing flowrate) the previous flow rate and intensity of destruction are smaller, therefore the structural parameter and the corresponding pressure drop is greater as compared with the down-phase at the same flow rate. Observable hysteresis therefore exists only if the flow rate changes significantly during the mean residence time ($t_{RTD} = L/\bar{u}$). At a high flow rate, the residence time is very short and the flow rate increase would have to be extremely high. The requirement for a maximum relative change of structural parameters during the mean residence time can be quantified as follows:

$$\frac{\Delta\lambda}{\lambda} \approx t_{RTD} \qquad (10)$$

For the analysed case (and for the model parameters shown in Figure 3) the $\Delta\lambda/\lambda$ ratio reaches the value of

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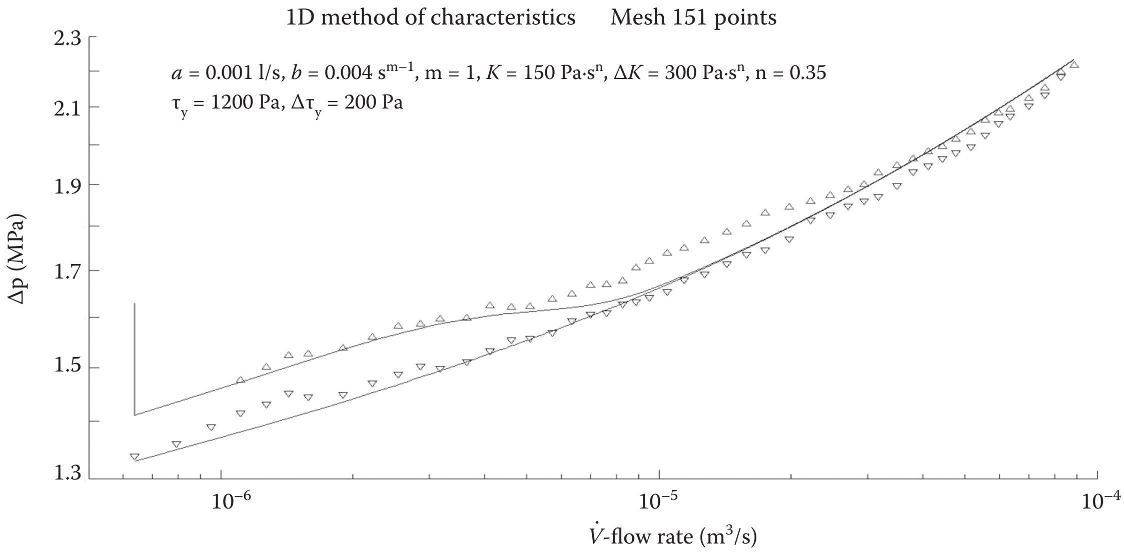

Figure 3. Hydraulic characteristic of collagen. Upward pointing triangles represent increasing flow rate; while downward pointing triangles represent decreasing flow rate. Continuous line integral model for R = 0.0106 m, L = 4.2 m, time up (1200 s)

about 100 at the minimum flow rate, and only about 0.01 at the maximum flow rate. This corresponds to the very long mean residence time at small flow rate, more than 2000 s, while at the highest flow rate the mean residence time is only 30 s and during this time the flow rate and the deformation history of fluid particles is changed only little.

CONCLUSIONS

The 1D method of characteristics was designed to simulate the transient flow of thixotropic incompressible liquids in pipes using the Houska model with variable yield stress. The model is robust, fast and can be implemented as control software in production lines with thixotropic foods. The developed model was used to evaluate the hydraulic characteristic of animal collagenous matter flowing in a long pipe. The phenomenon resembling hydraulic hysteresis was observed many times in a production line facility and this paper is an attempt to explain this behaviour by thixotropy. However, the hysteresis can be attributed to thixotropy only at low flow rates and hysteresis observed at high flow rates would need a different explanation.

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